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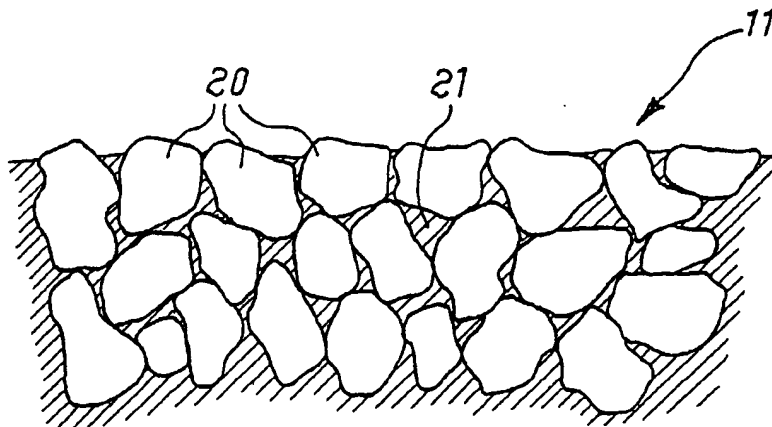
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- (71) Applicant (for all designated States except US): SAES GETTERS S.P.A. [IT/IT]; Viale Italia, 77, I-20020 Lainate (IT).
- (72) Inventors; and
- (75) Inventors/Applicants (for US only): BOFFITO, Claudio [IT/IT]; Via Papa Giovanni XXIII, 2, I-20017 Rho (IT). TOIA, Luca [IT/IT]; Via della Fontana, 14/A, I-21040 Carnago (IT). GALLITOGNOTTA, Alessandro [IT/IT]; Via Marconi, 52, I-21040 Origgio (IT).
- (74) Agents: PIZZOLI, Antonio; Società Italiana Brevetti S.p.A., Via Carducci, 8, I-20123 Milano et al. (IT).
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(54) Title: CATHODES FOR CATHODIC DEPOSITION OF GETTER ALLOYS AND A PROCESS FOR THE MANUFACTURE THEREOF



(57) Abstract: Composite cathodes for cathodic deposition of getter alloys are described, which are formed of powders of a getter alloy (20) in a matrix of a cementing component (21). Further, a process for the manufacture of said cathodes is described.

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"CATHODES FOR CATHODIC DEPOSITION OF GETTER ALLOYS AND A
PROCESS FOR THE MANUFACTURE THEREOF"

The present invention relates to cathodes to be used in the cathodic
5 deposition of getter alloys and to the process for the manufacture of these cathodes.

Getter materials are used for removing gases such as oxygen, hydrogen, water and carbon oxides in vacuum, in applications such as television and computer kinescopes, field emission-type flat displays (also known as FED), and
10 metal or glass interspaces for thermal insulation. Getter materials can also be used for removing the above gases from other gases such as nitrogen or rare gases, for example in order to keep constant the composition of the working atmosphere of devices such as lamps (mainly fluorescent ones), plasma displays or microelectronic circuits.

15 Getter materials can be pure metals, mainly zirconium, titanium, niobium, vanadium and tantalum; or alloys, mainly based on zirconium or titanium.

Some of the applications of getter materials require the manufacture of miniaturized getter devices, and particularly of devices having low thickness, of the order of a few microns. In some cases, the miniaturized getter device can be
20 produced separately and then inserted into the final device; it is mainly the case of getters inside the package of microelectronic circuits, or, for example, laser amplifiers for communications on optical fibers. In other applications the getter device must be produced simultaneously with other components of the final device, such as for example in some kind of FEDs, wherein "islands" of getter
25 material are spread over the whole surface of the display and are exposed to the internal evacuated space; or in the ferroelectric memories of computers, wherein getter material deposits are "embedded" in the structure of the device for protecting the ferroelectric material (generally a ceramic) from the contact with hydrogen which in time would affect its functionality

30 Particularly when the manufacture of the getter device has to be integrated with that of the final device, it is desirable to use the same techniques used for the

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manufacture of other components of the latter.

One of the techniques most commonly used in the manufacture of miniaturized devices is cathodic deposition.

As it is well known, a vacuum chamber wherein it is possible to create an electric field is used in this technique. In the chamber are placed a target (having generally the shape of a short cylinder) of the material which is to be deposited and, in front of the target, the support on which the thin layer is to be formed. The chamber is first evacuated and then backfilled with a noble gas atmosphere, generally argon, at a pressure in the range 10^{-3} - 10^{-5} mbar. By applying a potential difference of a few thousand of volt between the support and target holders (so that the target is at cathodic potential), a plasma of electrons and Ar^+ ions is created; these ions are accelerated from the electric field towards the target thus causing its erosion by impact. The species (generally atoms or "clusters" of atoms) derived from the erosion of the target are deposited on the support (as well as on the other available surfaces) thus forming the thin layer. In a variant of the method which is commonly used, a magnetic field is applied to the plasma zone, which helps to confine the plasma itself and improves the features of erosion of the cathode and of deposit formation; this variant is defined in the field as "magnetron". The deposit can cover the surface of the support completely, thus obtaining a single continuous deposit, or partially, obtaining deposits only on some zones of the support.

Since the target is maintained at the cathodic potential, it is also indicated in the field as "cathode", name which will be used in the rest of the description. The most commonly used cathodes have the shape of a disk, with diameter varying between about 2 and 30 cm and thickness varying between a few millimeters and about 20 cm, but in some applications also cathodes having other shapes (for example rectangular) and size are used.

The production of layers of getter materials by cathodic deposition is described in a number of patent publications. Patent application EP-A-572170 describes a use of the technique for the production of getter metal deposits such as Zr or Ti in field emission displays. Patent application EP-A-837502 describes the

production of layers of hydrogen getters, formed of nickel, palladium, platinum or oxides thereof by cathodic deposition. Finally, patent US 5,921,461 describes the production of getter material deposits to be used in the containers of microelectronic devices, indicating as preferred getter materials the metals
5 tantalum, titanium or molybdenum.

All these publications refer to the production of getter layers of pure metals. However, it is known that getter alloys have better gas sorption features than pure metals.

The production of alloys by cathodic deposition can be carried out starting
10 from several different cathodes, one for each component element of the alloy. However, since every metal has different features of erosion by the Ar^+ ions, it is difficult by this method to control the composition of the produced alloy. Therefore, it is certainly preferable to start from a single cathode. The various methods that, in principle, could be used for producing a cathode of getter alloy
15 have some drawbacks. A first possibility is producing an ingot by casting a melt having the composition of the desired alloy; however in most cases the cathode has then to be mechanically worked, in order to clean it from fusion slags or to adapt it to the size of the holder in the deposition chamber and, considering the fragility of the alloys, nearly all the cathodes break during these workings.
20 Another possibility is the production of an ingot by sinterization of powders of getter alloy; however, the getter alloys are difficult to be sintered by compression and subsequent thermal treatment and cathodes prepared in this way have nearly always a low mechanical resistance and break easily during transport or mounting in the deposition chamber.

25 Object of the present invention is providing cathodes for the cathodic deposition of getter alloys, as well as a process for the manufacture thereof.

The first object is obtained according to the present invention by a cathode made of a composite material, formed of:

- powders of a getter alloy; and
- 30 - a cementing component formed of a titanium or zirconium alloy with at least one element selected among iron, cobalt, nickel and copper;

wherein the weight of the getter alloy is between about 50% and 90% of the total weight of the cathode and wherein the cementing component has a melting point lower than that of the getter alloy.

The invention will be described in the following with reference to the accompanying drawings wherein:

- fig. 1 shows a cathode according to the present invention;
- fig. 2 shows in section an enlarged view of the surface of the cathode of figure 1; and
- fig. 3 shows a step of the manufacture process of the cathodes according to the invention.

Figure 1 represents a cathode 10 according to the invention, shaped as a disk; this cathode can have the typical size that was said before. Cathode 10 has a main surface 11, which is the one subjected to erosion during the deposition of the getter alloy layer.

Figure 2 shows in section an enlarged view of a portion of surface 11. The cathodes according to the invention are made of a composite material, and are formed of granules 20 of a getter alloy as the major component, and of a cementing component 21 as the minor component. The cementing component has the features of having in its turn a composition based on zirconium or titanium, thus similar to that of the getter alloys, and of having a melting point lower than the getter alloy and preferably lower than about 1000 °C. It has been found that the use of cementing components having compositions based on zirconium or titanium allows getter alloy deposits to be obtained that, although having a composition slightly different from that of the alloy which forms the cathode, have features of gas sorption which are essentially similar to the latter.

The getter alloy used in the cathodes of the invention can be any known getter alloy. Generally, binary alloys based on zirconium or titanium with one or more other components selected among aluminum, transition elements or rare earths are used; examples of said alloys are the binary alloys zirconium-vanadium, zirconium-iron, zirconium-nickel, zirconium-aluminum, titanium-vanadium and titanium-nickel; the ternary alloys zirconium-vanadium-iron and zirconium-

cobalt-rare earths; or alloys with more components.

Particularly suitable for the purposes of the invention are the alloys zirconium-aluminum described in patent US 3,203,901, and particularly the alloy having weight percent composition Zr 84% - Al 16%, produced and sold by the applicant with the name St 101; the alloys zirconium-nickel described in patent 5 US 4,071,335, and particularly the alloy having weight composition Zr 75.7%-Ni 24.3%, produced and sold by the applicant with the name St 199; the alloys zirconium-iron described in patent US 4,306,887, and particularly the alloy having weight composition Zr 76.6% - Fe 23.4%, produced and sold by the applicant with the name St 198; the alloys zirconium-vanadium-iron described in 10 patent US 4,312,669 and particularly the alloy having weight composition Zr 70%- V 24.6% - Fe 5.4%, produced and sold by the applicant with the name St 707; the alloys described in patent US 4,668,424, having composition zirconium-nickel-rare earths with optional addition of one or more other metals; the alloys titanium-vanadium-manganese described in patent US 4,457,891; and the alloys 15 zirconium-cobalt-rare earths described in patent US 5,961,750 and in particular the alloy of weight composition Zr 80.8% - Co 14.2% - rare earths 5%, produced and sold by the applicant with the name St 787.

The cementing component 21 is an alloy of titanium or zirconium with at 20 least one element selected among iron, cobalt, nickel and copper. The cementing component must have the feature of being more low-melting than the getter alloy, and preferably its melting temperature is lower than about 1000 °C. Suitable for the purposes of the invention are the alloys:

Zr-Fe having a zirconium weight content between about 81.5 and 86%, and 25 preferably of about 83%;

Zr-Co having a zirconium weight content between about 80 and 86%, and preferably of about 85%;

Zr-Ni having a zirconium weight content between about 81 and 84%, and preferably of about 83%;

30 Zr-Cu having a zirconium weight content between about 8.5 and 15% or between about 43 and 80%, and preferably the alloy having zirconium weight

content of about 53%;

Ti-Fe having a titanium weight content of about 67%;

Ti-Co having a titanium weight content of about 73%;

5 Ti-Ni having a titanium weight content between about 62 and 74%, and preferably of about 72.5%;

Ti-Cu having a titanium weight content between about 8 and 56%, and preferably of about 21%.

In case that the use of the cathode in the previously defined "magnetron" mode is foreseen, it can be preferable to use a cementing component based on
10 copper and not containing the magnetic elements iron, cobalt or nickel, which could interfere with the process.

The weight of the getter alloy is between 50% and 90% of the total weight of the cathode. With contents of alloy higher than 90% there is too little cementing component, and the mechanical resistance of the cathode decreases,
15 while for contents of getter alloy lower than about 50% there is an excessive quantity of cementing component which can lead to a composition of the getter layer deposited sensibly different from that of the starting getter alloy. Preferably the weight of the getter alloy in the cathode is comprised between about 70 and 85%.

20 The getter alloy is present in the cathode in powder with granules 20 having size comprised between about 50 and 200 μm , whereas the cementing component 21 forms a continuous matrix which binds the granules of the getter alloy.

In a second aspect thereof the invention relates to a process for the manufacture of the previously described cathodes.

25 The process will be described with reference to figure 3, which shows an important step thereof. A mechanical mixture, 30, of powders 20 of the getter alloy and powders 31 of the cementing component is used as starting material of the process; in the drawing the size of the granules 20 of the alloy is increased for the sake of clarity. The mixture 30 is introduced in a mould of suitable shape for
30 the manufacture of the cathode 10 and brought to a temperature higher than the melting temperature of the cementing component but lower than the melting

temperature of the getter alloy; in this operation the cementing component melts, thus forming a liquid that wets the granules of the getter alloy 20. Subsequently, the assembly is allowed to cool and the cementing component solidifies, thus forming a substantially cylindrical body formed of the matrix 21 which
5 conglomerates the granules 20, which can form the cathode 10 itself or a precursor thereof.

The two components 20 and 31 are mixed in the weight ratio corresponding to the desired percentage of getter alloy in the final cathode. The granules of getter alloy, 20, have the above cited particle size, while the granules of the cementing
10 component, 31, have a size comprised between about 20 and 100 μm . It has been found that the use of a cementing component in powder form having an average particle size lower than that of the getter alloy allows to obtain more homogeneous cathodes which have better mechanical properties.

As it is shown in the drawing, the mould has been made in two portions, a
15 cylindrical portion 32 and a base 32', easily separable at the end of the process; this structure favors the cathode extraction from the mould. The walls of the container are made of a material which does not interact with the cementing component in the melted state; to this end it is possible to use graphite, refractories or metals such as for example molybdenum or iron, the latter being
20 preferred for its low cost; alternatively, it is possible to use other materials, by coating the surfaces which will come into contact with the melt with a material which is inert with respect to it.

The melting step is carried out by placing the mould containing the mixture 30 in a vacuum oven, with a pressure during the operation lower than 10^{-2} mbar.
25 In this way it is avoided the possibility that the getter alloy reacts with gases present in the working atmosphere, as well as the formation of cavities in the cathode due to gas bubbles.

During the melting step it is also possible to cover the mixture 30 with a weight, having an external diameter equal to the internal diameter of the mould
30 (this possibility is not shown in the drawing); this weight favors the achievement of a more planar and regular upper surface of the cylindrical body, protects the

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mixture from contact with traces of gases present in the melting oven and avoids the presence of residual porosity in the final product. The weight is made by the same measures and materials used for the mould.

The cylindrical body itself extracted from the mould can form the cathode
5 10; this cathode has the advantage of being easily machinable, for example by turning, in order to adapt it to the holder. Alternatively, the body extracted from the mould can form a precursor of the cathodes of the invention; as a consequence of the machinability of the composite materials formed of granules of getter alloy in the cementing matrix, a body having multiple height with respect to that of the
10 desired cathode can be produced; this body can be subsequently divided into several parts, with cuts parallel to each other and perpendicular to the body axis, thus obtaining several equal cathodes from a single fusion.

The cathodes according to the invention can be used for the production by cathodic deposition of layers of getter alloys on the most different substrates, such
15 as metals, semiconductors (among which mainly silicon), ceramics, glass and plastics. Moreover, these cathodes can be used in deposition processes which may imply the application of a magnetic field ("magnetron" mode) or not; in the first case, the use of cathodes with a cementing component based on copper is preferred.

20

CLAIMS

1. A composite cathode (10) for the cathodic deposition of getter alloys formed of:
 - powders of a getter alloy (20); and
 - a cementing component (21) formed of a titanium or zirconium alloy with at least one element selected among iron, cobalt, nickel and copper;wherein the weight of the getter alloy is between about 50% and 90% of the total weight of the cathode and wherein the cementing component has a lower melting point than that of the getter alloy.
2. A cathode according to claim 1 wherein the weight of the getter alloy is between about 70% and 85% of the total weight of the cathode.
3. A cathode according to claim 1 wherein the cementing component has a melting point lower than about 1000 °C.
4. A cathode according to claim 1 wherein the getter alloy is a binary alloy based on zirconium or titanium with one or more elements selected among aluminum, the transition elements or the rare earths.
5. A cathode according to claim 4 wherein the getter alloy has the weight percent composition of Zr 84% - Al 16%.
6. A cathode according to claim 4 wherein the getter alloy has the weight percent composition of Zr 75.7% - Ni 24.3%.
7. A cathode according to claim 4 wherein the getter alloy has the weight percent composition of Zr 76.6% - Fe 23.4%.
8. A cathode according to claim 4 wherein the getter alloy has the weight percent composition of Zr 70% - V 24.6% - Fe 5.4%.
9. A cathode according to claim 4 wherein the getter alloy has the weight percent composition of Zr 80.8% - Co 14.2% - rare earths 5%.
10. A cathode according to claim 1 wherein the cementing component is a Zr-Fe alloy having a zirconium weight content comprised between about 81.5 and 86%.
11. A cathode according to claim 10 wherein said zirconium weight content is about 83%.
12. A cathode according to claim 1 wherein the cementing component is a Zr-Co

alloy having a zirconium weight content comprised between about 80 and 86%.

13. A cathode according to claim 12 wherein said zirconium weight content is about 85%.
14. A cathode according to claim 1 wherein the cementing component is a Zr-Ni alloy having a zirconium weight content comprised between about 81 and 84%.
15. A cathode according to claim 14 wherein said zirconium weight content is about 83%.
16. A cathode according to claim 1 wherein the cementing component is a Zr-Cu alloy having a zirconium weight content comprised between about 8.5 and 15%.
17. A cathode according to claim 1 wherein the cementing component is a Zr-Cu alloy having a zirconium weight content comprised between about 43 and 80%.
18. A cathode according to claim 17 wherein said zirconium weight content is about 53%.
19. A cathode according to claim 1 wherein the cementing component is a Ti-Fe alloy having a titanium weight content of about 67%.
20. A cathode according to claim 1 wherein the cementing component is a Ti-Co alloy having a titanium weight content of about 73%.
21. A cathode according to claim 1 wherein the cementing component is a Ti-Ni alloy having a titanium weight content comprised between about 62 and 74%.
22. A cathode according to claim 21 wherein said titanium weight content is about 72.5%.
23. A cathode according to claim 1 wherein the cementing component is a Ti-Cu alloy having a titanium weight content comprised between about 8 and 56%.
24. A cathode according to claim 23 wherein said titanium weight content is about 21%.
25. A cathode according to claim 1 wherein the getter alloy granules have size comprised between about 50 and 200 μm .
26. A process for the manufacture of cathodes for the cathodic deposition of getter alloys, comprising the steps of:
 - preparing a mechanical mixture (30) of powders of the getter alloy (20) and of the cementing component (31);

- introducing the mixture in a mould having suitable shape for the manufacture of the cathode;
 - inserting the mould containing the mixture into a vacuum oven and evacuating the latter at a pressure lower than 10^{-2} mbar;
 - heating the mixture (30) at a higher temperature than the melting temperature of the cementing component but lower than the melting temperature of the getter alloy;
 - allowing the system formed of the granules of the getter alloy (20) and the melted cementing component to cool down to room temperature;
 - taking the composite body formed of the granules of the getter alloy in the matrix of the cementing component out from the mould.
27. A process according to claim 26, wherein the body taken out from the mould forms the cathode (10).
28. A process according to claim 26, wherein the body taken out from the mould is divided into several parts, each of which forms a cathode.
29. A process according to claim 28, wherein said body is divided into equal parts, each of which forms a cathode (10), with cuts parallel to each other and perpendicular to the body axis.
30. A process according to claim 26, wherein the mixture (30) is formed of powders of a getter alloy (20) having a particle size comprised between about 50 and 200 μm and of powders of a cementing component (31) having a particle size comprised between about 20 and 100 μm .
31. A process according to claim 26 wherein the mould is formed of a cylindrical wall (32) and a base (32'), which are easily separable.
32. A process according to claim 26 wherein the mould is made with a material which does not interact with the cementing component in the melted state.
33. A process according to claim 32 wherein the mould is made with a material selected among graphite, refractories, molybdenum or iron.
34. A process according to claim 26 wherein, during the melting step, the mixture (30) is covered with a weight having the external diameter equal to the internal diameter of the mould.

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35. A process for the cathodic deposition of getter alloys which uses a cathode according to claim 1.
36. A process according to claim 35 wherein during the cathodic deposition a magnetic field is applied to the zone of the plasma.
37. A layer of getter alloy produced according to the process of claim 35 on a substrate selected among metals, semiconductors, ceramics, glass and plastics.

Fig. 1

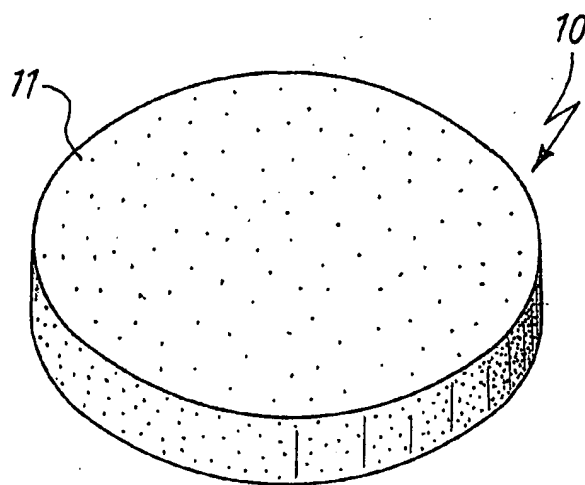


Fig. 2

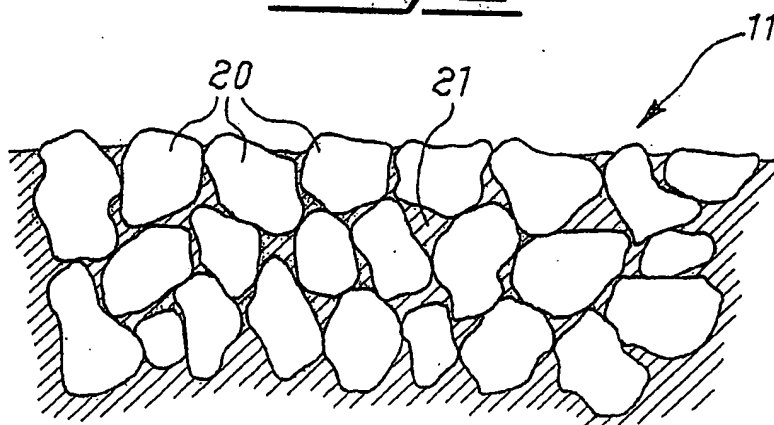
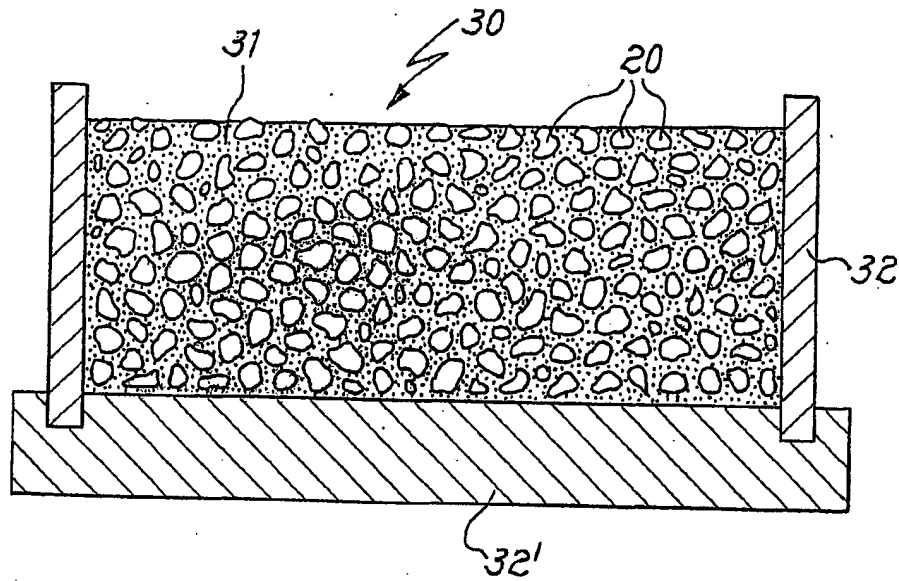


Fig. 3

INTERNATIONAL SEARCH REPORT

International Application No

PCT/IT 01/00332

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C23C14/34 C22C1/04 H01J7/18

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C23C C22C H01J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the International search (name of data base and, where practical, search terms used)

EPO-Internal, PAJ, WPI Data, INSPEC

C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category * | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
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☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Patterson, A

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

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